

KINETIC ANALYSIS OF THE CHLORINE ELECTRODE REACTION (CIER) ON Ti/RuO₂ BY MEANS OF THE POLARIZATION RESISTANCE

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The polarization resistance (R_p) of the CIER in chlorine saturated NaCl-HCl solutions was measured on Ti/RuO₂ electrodes varying the activity of chloride ions (a_{Cl^-}), the partial pressure of chlorine (p_{Cl_2}) and pH (or protons activity a_{H^+}). These results, which are free of interference related to porosity effects, were used for the kinetic analysis of the CIER mechanism.

It was verified that only in the range $0.3 < \text{pH} < 1$ the CIER is the main electrode reaction. In this domain, a linear dependence between R_p and a_{H^+} was observed (Figure 1). This behaviour was explained through the inhibition of active sites by protons according to the equilibrium $-SH^{Z+1} \leftrightarrow -S^Z + H^+$ [1], where $-S^Z$ is an active site for CIER and $-SH^{Z+1}$ represents the inhibited site. This model leads to an expression for the variation of R_p on pH, which describes appropriately the experimental results. It also allows to obtain the real polarization resistance (R_{p_o}), which can be simulated by the CIER kinetic mechanism.

On the basis of a complete kinetic analysis, the $R_{p_o} = f(a_{Cl^-}, p_{Cl_2})$ expressions were obtained for each one of the mechanisms under discussion at present [2]. The appropriate fitting of the R_{p_o} vs. a_{Cl^-} and R_{p_o} vs. p_{Cl_2} experimental results was achieved through a modification of the Volmer-Krishtalik mechanism, which involves the following steps:

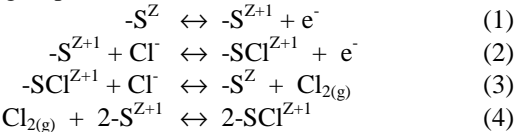


Figure 2 shows the experimental R_{p_o} vs. p_{Cl_2} dependencies as well as the corresponding correlations at three different concentrations of chloride ions. The resulting parameters were practically the same in each one of these, and the mean values are presented in Table 1. In Figure 3 the experimental and fitted R_{p_o} vs. a_{Cl^-} dependencies are shown, as well as the curve simulated using the constants in Table 1. It is verified a remarkable coincidence between them.

These results are a very strong evidence that the CIER on RuO₂ operates through the proposed mechanism, provided that it was able to describe different experimental runs obtained independently, with a unique set of values for the elementary step parameters.

Table 1. Elementary step parameters obtained by fitting R_{p_o} vs p_{Cl_2} experimental data. T = 30°C. $k_{\pm i}$ in mol s⁻¹cm⁻².

Step i	k_{+i}	k_{-i}	K_i
1	$1,23.10^{-11}$	$1,458.10^{17}$	$8,44.10^{-29}$
2	$6,98.10^{-15}$	955,03	$7,31.10^{-18}$
3	$6,89.10^{-11}$	$6,68.10^{-11}$	1,031
4	206,33	$2,67.10^{-9}$	$7,728.10^{10}$

[1] L. Koopal, *Electrochim. Acta* **41** (1996) 2293-2306.
 [2] S. Trasatti, *Electrochim. Acta* **32** (1987) 369-382.

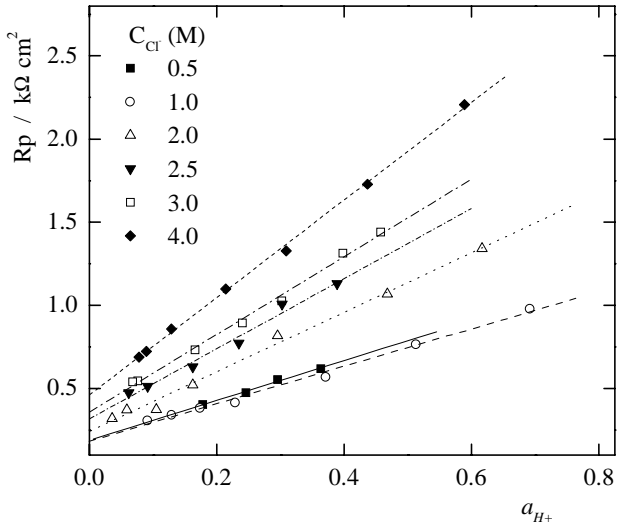


Figure 1. R_p vs. a_{H^+} dependencies in chlorine saturated (1 atm) NaCl - HCl solutions. T = 30°C.

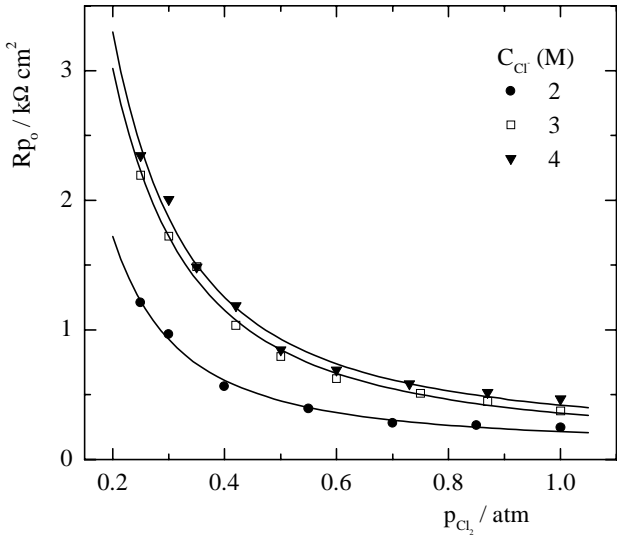


Figure 2. Experimental (points) and fitted (lines) R_{p_o} vs. p_{Cl_2} dependencies in chlorine saturated NaCl-HCl solutions. T = 30°C.

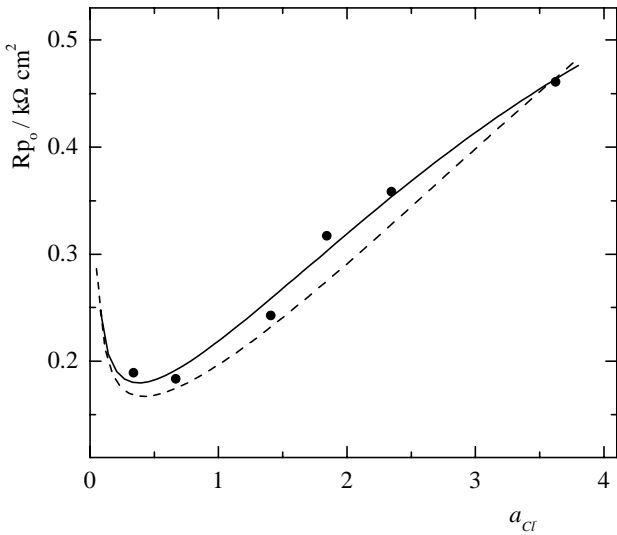


Figure 3. Experimental (points), fitted (solid line) and simulated (dashed line) R_{p_o} vs. a_{Cl^-} dependencies in chlorine saturated (1 atm) NaCl-HCl solutions. T = 30°C.